

Unit 6.3 Electronic spectroscopy (Marks 15)

Electronic transitions and selection rule - spectrum of atomic hydrogen – fine structure, spectra of H-like atoms.

Electronic transitions in diatomic molecules – Selection rule - Born Oppenheimer approximation – vibrational coarse structure - Frank Condon principle – electronic transitions in polyatomic molecules.

Structure elucidation by electronic spectroscopy – chromophore, auxochrome –absorption due to ethylenic chromophore – Woodward's rule. Electronic transitions in conjugated polyenes from particle in a box model. Effect of solvents on electronic transition, quantitative estimation by spectrophotometry.

Introduction to photoelectron spectroscopy and its applications in simple diatomic molecules.

Spectrum of Atomic Hydrogen

When an electric discharge is passed through gaseous hydrogen, the H₂ molecules are dissociated and the energetically excited H atoms that are produced emit light of discrete frequencies, producing a spectrum of a series of 'lines' (Fig. 10.1).

$$\tilde{\nu} = R_{\text{H}} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad R_{\text{H}} = 109\,677 \text{ cm}^{-1} \quad (10.1)$$

with $n_1 = 1$ (the Lyman series), 2 (the Balmer series), and 3 (the Paschen series), and that in each case $n_2 = n_1 + 1, n_1 + 2, \dots$. The constant R_{H} is now called the **Rydberg constant** for the hydrogen atom.

Spectrum of Atomic Hydrogen

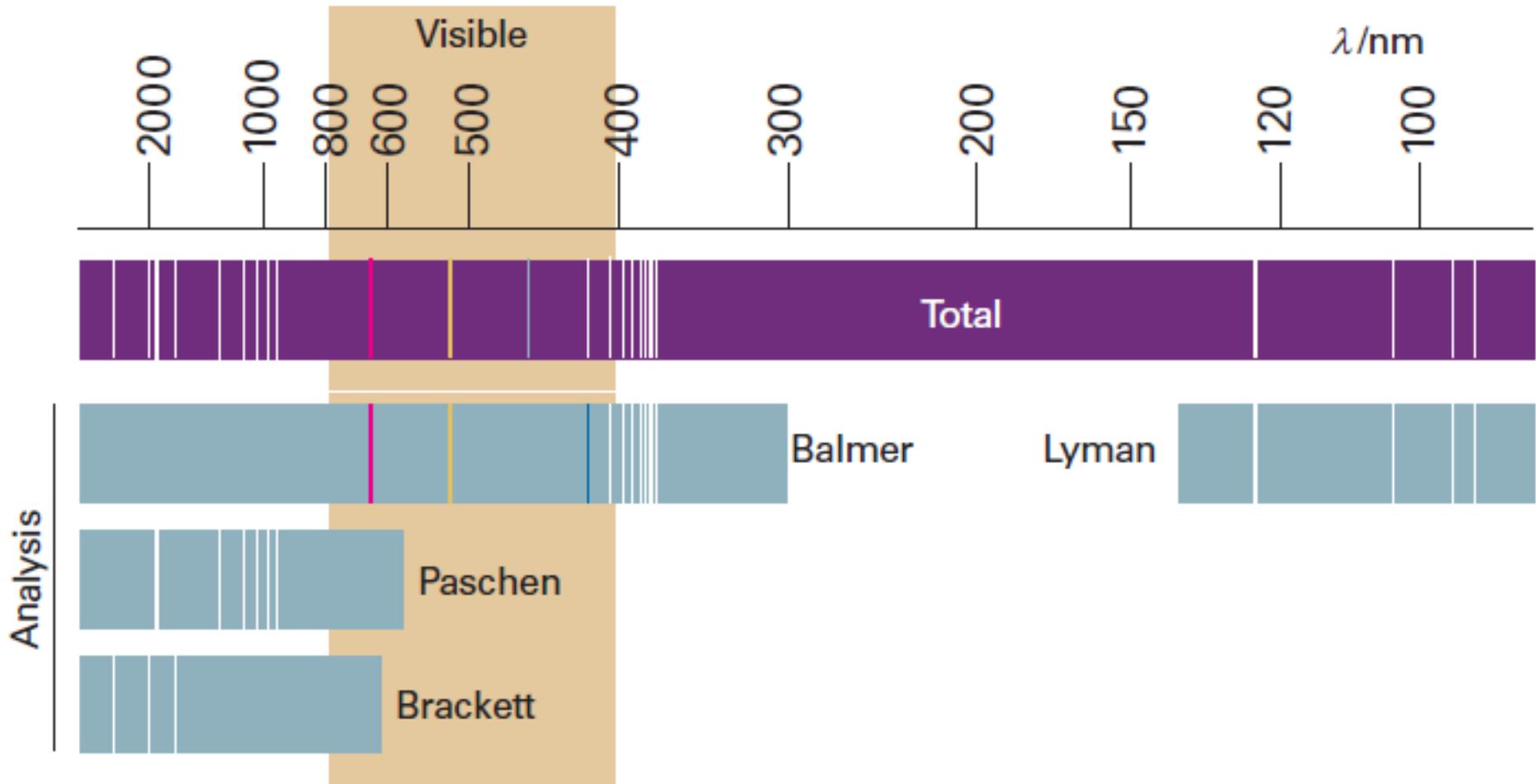


Fig. 10.1 The spectrum of atomic hydrogen. Both the observed spectrum and its resolution into overlapping series are shown. Note that the Balmer series lies in the visible region.

Spectroscopic Transition and Selection Rules

$$E_n = -\frac{Z^2 \mu e^4}{32\pi^2 \epsilon_0^2 \hbar^2 n^2} \quad (10.11)$$

The energies of the hydrogenic atoms are given by eqn 10.11. When the electron undergoes a **transition, a change of state, from an orbital with quantum numbers n_1, l_1, m_{l1} to another (lower energy) orbital with quantum numbers n_2, l_2, m_{l2}** , it undergoes a change of energy ΔE and discards the excess energy as a photon of electromagnetic radiation with a frequency ν given by the Bohr frequency condition

$$\Delta E = h\nu$$

Spectroscopic Transition and Selection Rules

It is tempting to think that all possible transitions are permissible, and that a spectrum arises from the transition of an electron from any initial orbital to any other orbital. However, this is not so, because a photon has an intrinsic spin angular momentum corresponding to $s = 1$. *The change in angular momentum of the electron must compensate for the angular momentum carried away by the photon.* Thus, an electron in a *d orbital* ($l = 2$) cannot make a transition into an *s orbital* ($l = 0$) because *the photon cannot carry away enough angular momentum.* Similarly, an *s electron cannot make a transition to another s orbital, because there would then be no change in the electron's angular momentum to make up for the angular momentum carried away by the photon.* It follows that some spectroscopic transitions are **allowed, meaning that they can occur, whereas others are forbidden,** meaning that they cannot occur.

Spectroscopic Transition and Selection Rules

A **selection rule is a statement about which transitions are allowed.** They are derived (for atoms) by identifying the transitions that conserve angular momentum when a photon is emitted or absorbed. The selection rules for hydrogenic atoms are

$$\Delta l = \pm 1, \Delta m_l = 0, \pm 1 \quad (10.26)$$

The principal quantum number *n* can change by any amount consistent with the Δl for the transition, because it does not relate directly to the angular momentum.

Color and Light Absorption of Compounds

Compounds that absorb light of wavelength between 400 and 800 nm (visible light) appear colored to the human eye, the precise color being a complicated function of which wavelengths the compounds subtract from white light. Very many compounds have strong ultraviolet absorption bands, the shoulders of which may tail into the visible spectrum-absorbing the violet end of the white-light spectrum. Subtraction of violet from white light leaves the complementary colors, which appear yellow/orange to the human eye, and for the same reason yellow and orange are the most common colors among organic compounds. Progressive absorption from 400 nm upward leads to progressive darkening through yellow, orange, red, green, blue, violet and ultimately black.

Chromophores

*Chromophore is a system responsible for imparting color to a compound. (The derivation is from the Greek *chromophoros*, or color carrier.) Thus, in azo dyes the aryl conjugated azo group (Ar- N= N- Ar) is clearly the principal chromophore; in nitro compounds the yellow color is carried by - NO₂; etc. The term has been retained within an extended interpretation to imply any functional group that absorbs electromagnetic radiation, whether or not a 'color' is thereby produced. Thus, the carbonyl group is a chromophore in both ultraviolet and infrared terms , even though one isolated C=O group is insufficiently 'powerful' to impart color to a compound. (An isolated carbonyl group, as in acetone , absorbs ultraviolet light around 280 nm.) Important examples of organic chromophores are listed in table 4.1.*

Chromophores

Table 4.1 Some simple organic chromophores and the approximate wavelengths at which they absorb. The intensity of absorption is discussed in section 4.2.2

<i>Chromophore</i>	<i>Wavelength, λ_{max}/nm (typical)</i>	<i>Intensity, $\epsilon_{max}/10^{-2}\text{m}^2\text{mol}^{-1}$ (typical)</i>
C=C	175	14 000
C≡C	175	10 000
	195	2 000
	223	150
C=O	160	18 000
	185	5 000
	280	15
R—NO ₂	200	5 000
	274	15
C≡N	165	5
C=C—C=C	217	20 000
C=C—C=O	220	10 000
	315	30
C=C—C≡C	220	7 500
	230	7 500
benzene	184	60 000
	204	7 400
	255	204

Auxochromes

An *auxochrome* was an earlier-defined term for a group that could enhance the color-imparting properties of a chromophore without being itself a chromophore, examples being -- OR, -NH₂, -NR₂, etc . As in the case of chromophores, the definition of auxochromes has been modified in the light of modern theory. The synergist effect of auxochromes is coupled with their ability to extend the conjugation of a chromophore by sharing of the nonbonding electrons: in a very real sense, the auxochrome then becomes part of a new, extended chromophore, and their action is only different in degree from the effect of extending the conjugation by adding a chromophore to a chromophore.

Theory of Electronic Transitions

When a molecule absorbs ultraviolet/visible light of a particular energy, we assume as a first approximation that only one electron is promoted to a higher energy level and that all other electrons are unaffected. The *excited state thus produced is formed in a very short time (of the order of 10^{-15} s)* and a consequence is that during electronic excitation the atoms of the molecule do not move (the Franck-Condon principle).

The most probable ΔE transition would appear to involve the promotion of one electron from the highest occupied molecular orbital to the lowest available unfilled orbital, but in many cases several transitions can be observed, giving several absorption bands in the spectrum. Not all transitions from filled to unfilled orbitals are allowed, the symmetry relationship between the two orbitals being important. Where a transition is 'forbidden', the probability of that transition occurring is low, and correspondingly the intensity of the associated absorption band is also low.

Theory of Electronic Transitions

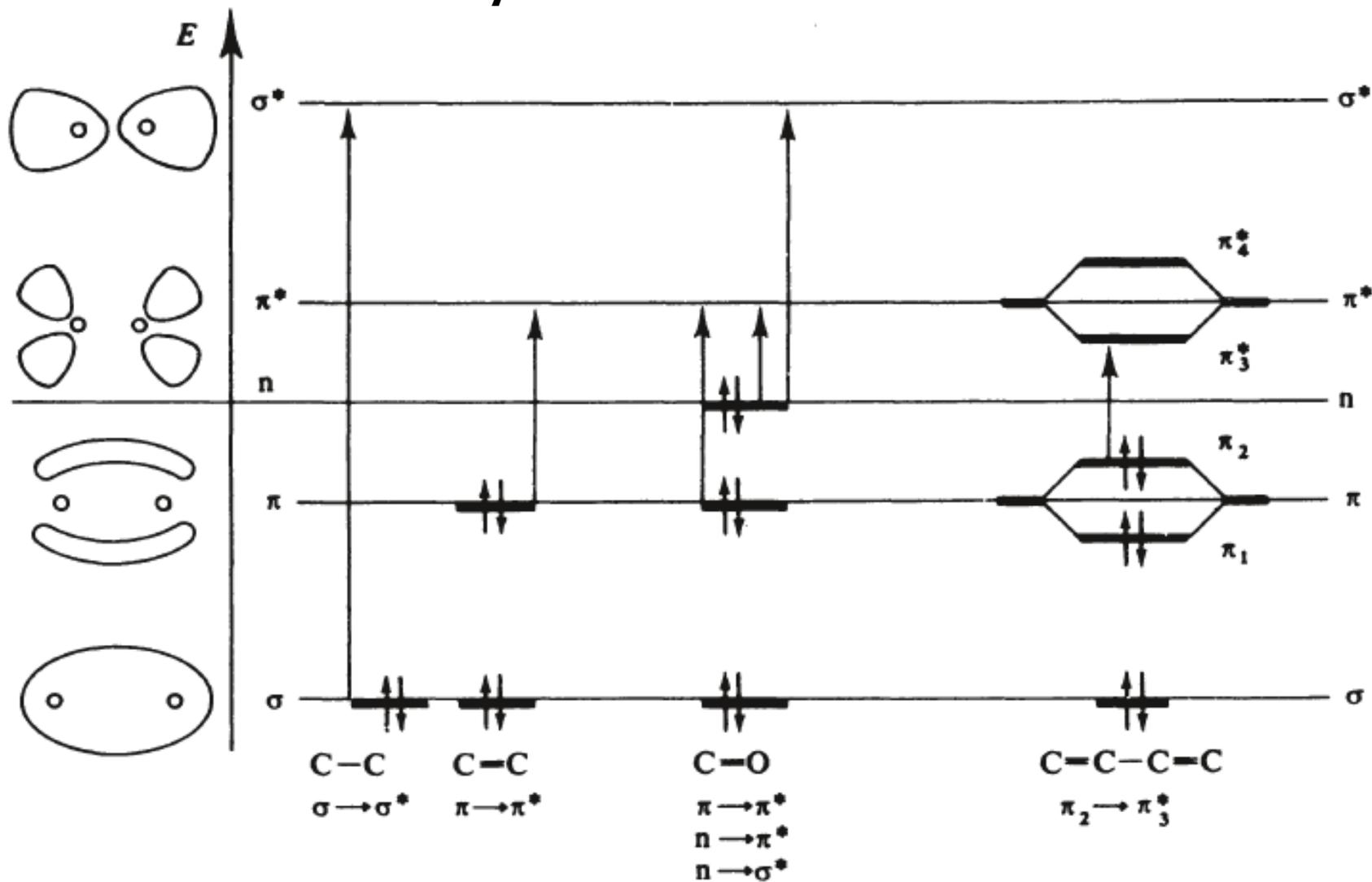


Figure 4.2 *Relative energies of orbitals most involved in electronic spectroscopy of organic compounds.*

Theory of Electronic Transitions

In alkanes the only transition available is the promotion of an electron from a low-lying σ orbital to a high-energy σ^* antibonding orbital: this is a high-energy process, and requires very short-wavelength ultraviolet light (around 150 nm). This type of transition is classed as $\sigma \rightarrow \sigma^*$.

In simple alkenes several transitions are available, but the lowest-energy transition is the most important: this is the $\pi \rightarrow \pi^*$ transition, which is responsible for the absorption band around 170-190 nm in unconjugated alkenes (see table 4.1).

In saturated aliphatic ketones the lowest-energy transition involves the non bonding electrons on oxygen, one of which can be promoted to the relatively low-lying π^* orbital: this $n \rightarrow \pi^*$ transition is 'forbidden' in symmetry terms and therefore the intensity is low, although the wavelength is long (around 280 nm). Two other transitions available are $n \rightarrow \sigma^*$ and $\pi \rightarrow \sigma^*$ these are both 'allowed' transitions and give rise to strong absorption bands, but the energy involved is higher than for $n \rightarrow \pi^*$; therefore, the wavelength of the absorption is shorter (around 185 for $n \rightarrow \sigma^*$ and around 160 for $\pi \rightarrow \pi^*$). The most intense band for these compounds is always due to the $\pi \rightarrow \pi^*$ transition

Theory of Electronic Transitions

In *conjugated dienes* the π orbitals of the separate alkene groups combine to form new orbitals—two bonding orbitals named π_1 and π_2 (or Ψ_1 and Ψ_2) and two antibonding orbitals named π_3^* and π_4^* (or Ψ_3^* and Ψ_4^*). The relative energies of these new orbitals are shown in figure 4.2 and it is easily apparent that a new $\pi \rightarrow \pi^*$ transition of very low energy ($\pi_2 \rightarrow \pi_3^*$) is now possible as a result of the conjugation. Conjugated dienes, therefore, show absorption at much longer wavelength than do isolated alkene groups, a typical value being around 217 nm. Table 4.1 also shows the wavelength of absorption for a typical conjugated ketone: again the strong absorption at 220 nm is the $\pi \rightarrow \pi^*$ transition, the weaker absorption being the forbidden $n \rightarrow \pi^*$ transition.

Theory of Electronic Transitions

